## PATENT SPECIFICATION

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## (54) FIXING OF HEAVY METALLIC COMPOUND

(71) We, NIPPON SODA COMPANY LIMITED, of No. 2-1, Ohtemachi 2-chome, Chiyoda-ku, Tokyo, Japan, a company organised under the laws of Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to fixing of heavy metal or heavy metallic compound and more particularly to treatment of a slurry or solution, or soil, containing heavy metal or heavy metallic compound to fix the metal or metallic compounds and thereby prevent same from dissolving in liquid, and to a construction cement having an agent to fix heavy metal or heavy metallic compounds.

In recent times the environment has been subject to pollution by heavy metals or heavy metallic compounds discharged from mines, factories, cars, hospitals, laboratories or derived from waste products such as electric batteries and lamps. These heavy metals or heavy metallic compounds dissolve in river or subterranean water, and may be absorbed by plants and animals and in turn by human beings.

According to a first aspect of the present invention, there is provided a method of treating a slurry or solution containing heavy metal or heavy metallic compound to fix the metal or metallic compound, comprising the step of mixing with the solution or slurry 0.1 to 50.0—by weight of an aliphatic dithiocarbamate compound, wherein the aliphatic dithiocarbamate compound is a compound having an aliphatic chain, which may contain a nitrogen atom in place of a carbon atom, and at least two dithiocarbamic acid groups

or alkali metal, alkaline earth metal or ammonium hydroxide salts or esters thereof.

The aliphatic dithiocarbamate compound may be present in a cement composition in an amount of 0.001 to 10% by weight of the composition, the composition being mixed in the slurry or solution in an amount of 20 to 80% by weight.

According to a second aspect of the present invention, there is provided a

According to a second aspect of the present invention, there is provided a method of treating soil containing heavy metal or metallic compound, to prevent plants from absorbing the metal or metallic compound, comprising the step of mixing in the soil 0.001 to 10% by weight of an aliphatic dithiocarbamate compound, wherein the aliphatic dithiocarbamate compound is a compound having an aliphatic chain, which may contain a nitrogen atom in place of a carbon atom, and at least two dithiocarbamic acid groups

or alkali metal, alkaline earth metal or ammonium hydroxide salts or esters thereof. Preferably, 0.01 to 2.0% by weight of the compound is mixed with the soil.

	According to a third aspect of the present invention, there is provided a construction cement having a heavy metal or heavy metallic compound fixing agent, the agent being present in an amount of 0.001 to 10% by weight and comprising a compound prepared by reacting an appropriate property of the present in an amount of 0.001 to 10% by weight and comprising a compound prepared by reacting an appropriate property of the present invention, there is provided a construction compound in the provided a construction of the present invention, there is provided a construction compound for the present invention, there is provided a construction compound fixing agent, the	
5	triamine, triethylene tetramine, tetracthylene pentamine, propylenediamine, dipropylenetriamine, tripropylene tetramine, tetracthylene pentamine, tetrapropylene pentamine and pentapropylenehexamine with carbon bisulfide, one gram molecule of amine to 2 to 6 gram molecules of carbon bisulfide being employed	5
10	dithiocarbamate compound is used as a fixing agent for heavy metals or heavy metallic compounds by being mixed with soil, water or slurry wastage containing heavy metal or heavy metallic compound. The fixing agent reacts with the heavy metal or heavy metallic compound to form a compound insoluble in water	10
15	This fixing agent can have less conventional usages, for example, when slurry or granular wastage containing heavy metals or heavy metallic compounds, such as mud containing a mercuric compound byproduct of an electrolysis plant, is packed in a concrete container and dumped in the sea or buried in the ground, heavy metals or heavy metallic compounds may be dissolved by water and exude through the wall of the container which results in pulled by water and exude through the wall	15
20	of the container, which results in pollution of the environment. In this case, mixing of the agent in the mud in an amount of 0.1 to 50% by weight may prevent the exudation of the heavy metal and heavy metallic compounds. Further, if the agent is homogeneously mixed in concrete or mortar in an amount of 0.001% to 10%, preferably 0.001 to 1% by weight, of the cement used in the concrete or mortar, the agent may prevent heavy metals and heavy metallic compounds from passing through the concrete or mortar.	20
25	the concrete or mortar. Moreover, setting material, which solidifies to be tough, for example, cement such as Portland cement or the raw material of a resin, and which contains 0.001% to 10%, preferably 0.001% to 1%, by weight of the agent, can be used for packing harmful heavy metallic compounds, and walls or other constructions, such as drainage pipes, made from such material may resist the passage therethrough of heavy metals and heavy metallic compounds.	25
.30	The agent may be used in agriculture, as when a soil contains a heavy metal or heavy metallic compound, crops planted in the soil may absorb the heavy metal or heavy metallic compound. In this case, the absorption of the heavy metal	30
35	heavy metallic compound by the crops may be prevented by adding the agent to the soil. Conveniently, 0.001 to 10%, preferably 0.01 to 2%, by weight of the agent is added and homogeneously mixed in the soil. The agent is effective, particularly when the soil has weak acidity of alkalinity of pH 5 to 11, against mercury, copper and cadmium. Moreover, heavy metal or heavy metallic compound in irrigation water may be precipitated by adding the agent to the water.	35
40	In the present invention, aliphatic dithiocarbamate compound means a compound having an aliphatic chain which may contain a nitrogen atom in place of a carbon atom and at least two dithiocarbamic acid groups	40
	(>N—C—S—H),    	
45	which is contained in the compound in the form of acids (RNHCSSH or R' NCSSH) or salts or contained in the compound in the form of acids (RNHCSSH)	
70	>NCSSH) or salts or esters of alkali metals, alkaline earth metals and ammonium R hydroxide of the dithiocarbamic acid groups.  The following are examples of aliphatic dithiocarbamate compounds that may be used:	45
50	ethylene-di-thiocarbamic acid (HS <sub>2</sub> CNHCH <sub>2</sub> CH <sub>2</sub> NHCS <sub>2</sub> H) N,N,N-tris(dithiocarboxyl)ethylenediamine N,N,N',N'-tetra(dithiocarboxyl)ethylenediamine 1,3- or 1,2-propylenebianoshamic acid N,N,N', tris(dithiocarbamic)	50
55	N,N,N'-tris(dithiocarboxyl)propylenediamine N,N,N'N'-tetra(dithiocarboxyl)propylenediamine tetramethylenebisdithiocarbamic acid tris or tetra-(dithiocarboxyl)propylenediamine hexamethylenebisdithiocarbamic acid octamethylenebisdithiocarbamic acid	55

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	N <sub>2</sub> N <sup>3</sup> -bis(dithiocarboxyl)diethylenetriamine	
	HS_CHNCH_CH_NHCH_CH_NHCS_H)	
	N <sup>1</sup> , N <sup>2</sup> , N <sup>3</sup> -tris(dithiocarboxyl)diethylenetriamine	
5	N¹,N¹,N²,N°-tetra(dithiocarboxyl)diethylenetriamine N¹,N¹,N²,N°,N°-penta(dithiocarboxyl)diethylenetriamine	_
•	N <sup>1</sup> ,N <sup>2</sup> -bis(dithiocarboxyl)triethylenetetramine	5
	(HS <sub>2</sub> CNHC <sub>2</sub> H <sub>1</sub> NHC <sub>2</sub> H <sub>1</sub> NHC <sub>2</sub> H <sub>1</sub> NHCS <sub>2</sub> H)	
	N', N2, N4-tris(dithiocarboxyl)triethylenetetramine	
	N <sup>1</sup> ,N <sup>2</sup> ,N <sup>3</sup> ,N <sup>3</sup> -tetra(dithiocarboxyl)triethylenetetramine	
10	N',N',N2,N3,N'-penta(dithiocarboxyl)triethyleneretramine	10
	N <sup>1</sup> ,N <sup>2</sup> ,N <sup>3</sup> ,N <sup>3</sup> ,N <sup>3</sup> -hexa(dithiocarboxyl)triethyleneretramine	
	N <sup>1</sup> ,N <sup>2</sup> -bis(dithiocarboxyl)tetraethylenepentamine	
	(HS <sub>2</sub> SNHC <sub>2</sub> H <sub>1</sub> NHC <sub>2</sub> H <sub>1</sub> NHCS <sub>2</sub> HC <sub>2</sub> H <sub>1</sub> NHC <sub>2</sub> H <sub>1</sub> NHCS <sub>2</sub> H)	
15	N <sup>1</sup> , N <sup>3</sup> , N <sup>5</sup> -tris(dithiocarboxyl) tetraethylenepentamine	
	N <sup>1</sup> , N <sup>2</sup> , N <sup>3</sup> , N <sup>5</sup> -tetra (dithiocarboxyl) tetraethylenepentamine	15
	N <sup>1</sup> , N <sup>2</sup> , N <sup>3</sup> , N <sup>4</sup> , N <sup>3</sup> -penta (dithiocarboxyl) tetraethylenepentamine	
	$N^1,N^2,N^3,N^4,N^5,N^5$ -hepta (dithiocarboxyl) tetraethylenepentamine $N^1,N^2,N^2,N^3,N^4,N^5$ -hexa (dithiocarboxyl) tetraethylenepentamine	
	N <sub>1</sub> ,N <sub>6</sub> -bis (dithiocarboxyl) pentaethylenehexamine	
20	N', N'3, N'6-tri (dithiocarboxyl) pentaethylenehexamine	20
	N1, N3, N4, N6-tetra (dithiocarboxyl) pentaethylenehexamine	20
	N <sup>1</sup> ,N <sup>2</sup> ,N <sup>3</sup> ,N <sup>4</sup> ,N <sup>6</sup> -hexa(dithiocarboxyl)pentaethylenehexamine	
	bis(dithiocarboxyl)propylenediamine	
	trisdithiocarboxyldipropylenetriamine	
25	$N^1$ , $N^2$ -bis(dithiocarboxyl) tripropylenete tramine	25
	N <sup>1</sup> ,N <sup>2</sup> ,N <sup>3</sup> -tris(dithiocarboxyl)tripropylenetetramine	
	N <sup>1</sup> ,N <sup>2</sup> ,N <sup>3</sup> ,N <sup>4</sup> -tetra (dithiocarboxyl) tripropylenetetramine	
	N <sup>1</sup> ,N <sup>2</sup> ,N <sup>3</sup> ,N <sup>4</sup> -penta(dithiocarboxyl)tripropylenetetramine	
20	N <sup>1</sup> ,N <sup>1</sup> ,N <sup>2</sup> ,N <sup>3</sup> ,N <sup>4</sup> ,N <sup>4</sup> -hexa(dithiocarboxyl)tripropylenetetramine	
30	N1,N5-bls(dithiocarboxyl)tetrapropylenepentamine	30
	N <sup>1</sup> ,N <sup>3</sup> ,N <sup>5</sup> -tris(dithiocarboxyl)tetrapropylenepentamine	
	N1, N2, N5, N5-tetra (dithiocarboxyl) tetra propylene pentamine	
	N <sup>1</sup> , N <sup>2</sup> , N <sup>3</sup> , N <sup>4</sup> , N <sup>5</sup> -penta (dithiocarboxyl) tetrapropylenepentamine	
35	N¹,N¹,N²,N³,N³,N³-hexa(dithiocarboxyl)tetrapropylenepentamine	
	N <sup>1</sup> ,N <sup>2</sup> -bis(dithiocarboxyl)dibutylenetriamine N <sup>1</sup> ,N <sup>2</sup> ,N <sup>3</sup> -tris(dithiocarboxyl)dibutylenetriamine	35
	N',N°-bis (dithiocarboxyl) tributylenetriamine	
	N <sup>1</sup> ,N <sup>2</sup> ,N <sup>3</sup> -tris(dithiocarboxyl)tributylenetriamine	
	N1,N4-bis(dithiocarboxyl)tetrabutylenepentamine	
40	N <sup>1</sup> ,N <sup>2</sup> ,N <sup>4</sup> -tris(dithiocarboxyl)tetrabutylenepentamine	40
	N <sup>1</sup> ,N <sup>2</sup> ,N <sup>3</sup> ,N <sup>4</sup> -tetra (dithiocarboxyl) tetrabutylenepentamine	-10
	poly(N-dithiocarboxyl)polyethyleneimine (polyethyleneimine have the following	
	structure:	
	( CII CII NI	
	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	
15	and alkali matal (a.g. No and V) attraling posts great (a.g. No No. Co. and	
	and alkali metal (e.g. Na and K), alkaline earth metal (e.g. Be, Mg, Ca and	45
	Ba) or ammonium hydroxide salts of above said acids, and the esters with the alcohols having 1 to 4 carbon atoms.	
	An aliphatic dithiocarbamate compound having less than 4 carbon atoms shows	
	phytotoxicity, so aliphatic dithiocarbamate compounds having 5 or more carbon atoms	
50	are preferred.	50
•	These dithiocarbamate compounds can be easily prepared from corresponding	50
	amine compounds such as ethylenediamine, diethylenetriamine, triethylenetetramine,	
	tetraethylenepentamine, pentaethylenehexamine, dipropylenetriamine, tripropylene-	
	tetramine, tetrapropylenepentamine, dibutylenetriamine, tributylenetriamine and tetra-	
5	butylenepentamine by reacting with carbon bisulfide in the presence of a solvent	55
	such as acetone, methylethyl ketone and water and alkaline catalysts such as sodium	
	hydroxide, potassium hydroxide and ammonium hydroxide, at a temperature of from	
	-10°C to 60°C, preferably 20°C to 45°C. The reaction mixture contains dithio-	
0	carbamate compound, which has a red-orange or brown colour, in the form of a salt.	
U	The reaction between the hydrogen atom which combines with the nitrogen atom of	60
	amino or imino group and carbon bisulfide proceeds quantitatively. Accordingly, the	

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	same number of gram molecules of carbon bisulfide as the proposed number of dithiocarbamate groups of the proposed compound is employed in its preparation.  For example, when two dithiocarbamate groups are intended to introduce in amine compound, two gram molecules of carbon bisulfide are reacted with one gram	
5	molecule of amine compound. Ordinarily, aliphatic dithiocarbamate compound can be used as a fixing agent in the form of an aqueous solution, or a carrier can be impregnated with the aqueous solution of aliphatic dithiocarbamate to provide a granular or paste fixing agent. In the latter case, 1 to 30% of the aliphatic dithiocarbamate compound is preferably contained in the carrier.	5
10	Many kinds of materials having a porous structure and large specific surfaces can be employed as the carrier, preferably porous material having a large specific surface of more than 1m <sup>2</sup> /g measured by argon gas adsorption method by use of the BET equation, for example, diatomaceous earth, pumice stone, zeolite, kaolin, vermiculite, alumina (aluminium oxide), silicagel, coke, activated charcoal, graphite, bento-	10
15	The fixing agent can selectively react with heavy metal and heavy metallic compounds such as nickel, chromium, zinc, lead, copper, cadmium, silver, arsenic, manganese, bismuth, vanadium and mercury, particularly mercury and compounds thereof, even if these heavy metals or metallic compounds exist as non-jonic or jonic	15
20	compounds. So far as concerns mecuric and silver compounds, various types of compound can be fixed, for example, metallic oxides such as HgO and Ag <sub>2</sub> O, metallic chlorides such as HgCl <sub>2</sub> and AgCl, metallic sulphates such as HgSO <sub>4</sub> , Hg <sub>2</sub> SO <sub>4</sub> and AgSO <sub>4</sub> , metallic nitrates such as Hg(NO <sub>2</sub> ) <sub>2</sub> and Hg <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> , metallic sulphides such as HGS and Hg <sub>2</sub> S, and organometallic compounds such as methylmercuric	20
25	chloride, ethylmercuric chloride, phenylmercuric acetate, ethylmercuric iodide, methylmercuric iodide, ethylmercuric bromide, methylmercuric fromide, phenylmercuric chloride, diphenylmercury and phenylmercuric benzoate are fixed.  Furthermore, cadmium and cadmium compounds can be fixed by the agent, even if the cadmium compounds are non-ionic or ionic, for example, CdSO <sub>4</sub> , CdCl <sub>2</sub> ,	25
30	CdS, CdO and Cd(OH) <sub>2</sub> .  Embodiments of the method and of the cement composition according to the present invention, and preparation of fixing agents employed in such embodiments, are illustrated by the following examples. All quantities referred to in the description and appended claims as "parts" or "percent" are "parts by weight" or "percent by	30
35	weight" respectively unless expressly stated otherwise.	35
40	Example 1.  Preparation of fixing agents.  80 parts of NaOH, 500 parts of water and 60 parts of ethylene diamine were mixed together, and 152 parts of carbon bisulfide were added dropwise at 30°C to 40°C under vigorous stirring. After 1 hour of the reaction, nitrogen gas was blown through the reaction mixture to remove any unreacted carbon bisulfide. A brown-orange transparent aqueous solution containing 31.0% of sodium ethylenebisdithio-carbamate (NaS2CNH—CH2CH2NHCS2Na) was obtained. The reaction solution itself was used as a fixing agent.	40
45	Examples 2 to 25.  Various kinds of amines, basic compounds and carbon bisulfide, as shown in Table 1, were reacted according to the procedure of example 1 and various kinds of fixing agents were obtained, the fixing agents and raw materials being listed in Table 1.	45
50	Example 26.  Aliphatic dithiocarboxyl compounds, identified by the numbers given in Table 1, Portland cement, water and mud containing mercuric compound byproduct from a sodium chloride electrolysis plant were mixed in the proportions given in Table 2 and allowed to solidify into blocks 16cm high × 4cm wide × 4cm long. The blocks	50
55	were allowed to stand for 14 days and then were soaked in quantities of pure water and sea water 4 times the volume of the blocks.  The concentration of mercury in the sea water or pure water was measured after periods of 1 hour, 1 day, 14 days, 1 month and 1 year. The results are listed in Table 2.	55
60	The mud originally contained NaCl, Mg(OH) <sub>2</sub> , CaSO <sub>4</sub> : 2H <sub>2</sub> O, CaCO <sub>3</sub> , C, about 120 ppm of mercury and about 45% water.	60

TABLE 1

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nt		note	needle crystal	needle crystal	1	1	l	_		-	reaction product of example 5 was treated with acid
reaction product of fixing agent	aliphatic dithio carbamate	compound (%)	sodium ethylenebisdithio carbamate (31)	Calcium ethylenebisdithio carbamate (31)	tris(dithiocarboxyl sodium) diethylenetriamine (37)	tris(dithiocarboxyl calcium) diethylenetriamine (36)	tetra(dithiocarboxyl sodium) triethylenetetramine (36)	tetra(dithiocarboxyl calcium) triethylenetetramine (28)	penta(dithíocarboxyl sodium) tetraethylenepentamine (34)	poly n-dithiocarboxyl sodium polyethyleneimine (21)	tetra(dithiocarboxyl sodium) triethylenetetramine (35)
		color	brown S orange	orange	brown S orange	pale yellow S green	brown S orange	pale yellow	orange	orange	orange
		(၁၀)	40	45	40	43	40	45	40	43	40
		temp (°C)	30	es S	30	20	77	25	15	28	30
		CS2	152	152	228	228	304	304	380	09	228
	ırts)	water	200	200	500	500	800	700	1200	300	800
	ıls (pa		08	74	120	74	160	74	200	32	160
	raw materials (parts)	alkali	NaOH	Ca(OH),	NaOH	Ca(0H)2	NaOH	Ca(OH),	NaOH	NaOH	NaOH
	_		09	09	103	103	146	146	681	30	146
		amine	e thy lenediamine	ethylenediamine	diethylene- triamine	diethylene- triamine	triethylene- tetramine	triethylene- tetramine	tetraethylene pentamine	polyethylene- iminc (m.w. = 1,000)	triethylene- tetramine
		examp. No.		2	3	4	۶.	9	7	<b>6</b> 0	6

TABLE 1 (Continued)

	т		<del>~</del>	·							
111		note	reaction product of example 8 was treated with acid	reaction product of example I was treated with ZnC1,		needle crystal	needle crystal	needle crystal		block crysta!	block crystal
reaction product of fixing agent	a linkatic distriction	compound (%)	poly n-dithiocarboxyl polyethyleneimine (20)	zinc ethylencbisdithio carbanate (28)	mixture of tetra and tri- (dithiocarboxyl sodium) diethylenetriamine (33)	N.N.N.,Ntetra(dithiocarboxyl sodium) ethylenediamine	N', N', N', N', N', N'-hexa (dithio- carboxyl sodium) triethylene teframine	N',N',N2,N3,N4,N4,N5-hepta(di- thiocarboxyl sodium)tetrapen- tamine	N.N¹-di(thiocarboxyl sodium) diaminopropane	N,N'-di(dithiocarhoxy! sodium)	N,N <sup>1</sup> -di(dithiocarboxyl sodium) octamethylenediamine
		color	orange	pale orange	pale red	orange	yellow S orange	orange	orange	orange	Orange O
		(oC)	40	40	<del>\$</del>	45	45	45	45	45	45
		temp (°C)	15	30	50	30	30	30	æ	30	30
		CS <sub>2</sub>	380	153	342	304	456	532	152	55	152
	arisi	water	1200	200	500	800	0001	1200	5.20	009	700
	साठ क्षे		32	80	160	160	240	280	980	08	80
	iaw materiats (parts)	alkali	NaOH	NaOII	NaOI I	NaOH	NaOH	NaOII	NaOH	NaOH	NaOH
			30	99	103	09	146	681	7.4	116	4
		สถานิ	polyethylene mine	ethylene- diamine	diethylene- triamine	ethy lenethamine	tric thy lene- tetramine	tetraethylene pentamine	1,3-diamino- propane	hexamethy lene diamine	Octamethy lene diamine
	examin	Ŋ,	2	=		13		1.5	16	11	200

TABLE 1 (Continued)

										reaction product of fixing agent	
		ä	raw materiais (parts)	s (pari	ts)			4		aliphatic dithin carbamate	
examp. No.	атіпе		alkali		water	CS,	temp (°C)	(၃)	color	compound (%)	note
61	1,3-diamine- propane	74	NaOH	160	700	304	30	45	orange	N,N,N',N'-tetra(dithiocarboxy) sodium)1,3-diaminopropane	block crystal
20	hexamethylene- diamine	116	NaOH	160	800	304	30	45	оганде	N,N,N',N'-tetra(dithiocarboxv1 sodium)hexamethylenediamine	block crystal
21	diethylene- triamine	103	Ca(OH)2	74	200	152	30	40	orange	N', N3-bis (dithiocarboxyl calcium) diethylenetriamine	-
23	triethy lene- tetramine	146	Ca(OH)2	74	200	152	30	.40	orange	N <sup>4</sup> ,N <sup>4</sup> -bis(dithiocarboxyl calcium) triethylenetetramine	
23	diethylene- triamine	103	NaOH	80	500	152	30	40	orange	N <sup>4</sup> ,N <sup>3</sup> -bis(dithiocarboxyl calcium) diethylenetriamine	
24	tetraethylene pentamine	189	NaOH	200	200	380	30	9	orange	N', N <sup>s</sup> -bis (dithiocarboxyl sodium) tetraethylene pentamine	
25	triethylene tetramine	146	NaOH	80	500	152	30	Q+	orange	N',N'-bis(dithiocarboxy) sudium) triethylene tetramine	

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		agent (narts)			o Bij	ilg concentution (ppm)	.ppm)	
(parts) No.s o	~ c .	No.s of Table 1	test water	1 hour	1 day	14 days	1 month	I year
No 5 (0 001)	=	0.00	water	not	กดเ	not	пол	not
	3	(100:	sea water	detected*	detected	detected	detected	detected
7 No 3 (0.01)	5	90	water	33	**	, 11	1.1	**
	į		sea water	10	"	14	11	:
No 7 (0 005)	9	טטפו	water		+	11	16	Ξ
	1	(***)	sea water	:	::	14		:
No. 10 (0.01)	9	110	water	*	13	13	,	:
		, , ,	sea water	33		"		-
2 No. 11 (0.02)	9	(21	water	:	:			
		į	sea water		.,	:	:	:
2 No. 13 (0.03)	9	(3)	water				"	:
_			sea water		33		Ξ	
2 No. 15 (0.005)	٤	1003	water			11	:	:
	1		sea waler	3.1	1.	:	:	
2 No. 17 (0.01)	9	(10	water	**	14	**		
_	;		sea water	:	:	:	=	÷

TABLE 2 (Continued)

										-
····					Hg	Hg concentration (ppm)	(ppm)			
water (parts)	mud (parts)**	cement (parts)	fixing agent (parts) No.s of Table i	test water	1 hour	1 day	14 days	I month	1 year	
1				water	not	not	not	not	not	
	¢)	7	No. 18 (0.01)	sea water	detected*	detected	detected	detected	detected	
1				water		.,		11	-	
	63	۲۱	No. 19 (0.01)	sea water	:	8.6	64	11		
			none	water	0.009	0.015	0.042	0.068	0.21	
l (control)	73	:4	none	sea water	0.005	0.007	0.016	0.022	0.15	

\* less than 0.001 ppm

\*\* day weight

Example 27.

500 parts of dry sludge containing copper and copper compound byproducts from a copper electro plating factory and 0.5 part of tetra (dithio carboxyl sodium) triethyleneteramine (No. 5 in Table 5) were mixed together and 25 parts of epoxide resin and 25 parts of curing agent (amines) were admixed with the mixture. The resulting mixture was cured in moulds to produce test blocks each of 4cm × 4cm × 4cm.

The test blocks were soaked in quantities of sea water and pure water 4 times the volume of the blocks. At periods of 1 day, 1 month and 3 months, the copper concentration in the sea water or pure water was measured, and the results are listed in Table 3.

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TABLE 3

		т—	T		<del></del>	,
	(mdd)	3 months	not detected	*	1.5	THE CT
	copper concentration (ppm)	I month	not detected	:	0.23	0,46
	addon	i day	not detected *	•	1.4	4.
ו שחמעו		lest water	wafer	sea wafer	water	sea water
_		shidge	003		005	
	composition (parts)	fixing agent	tetra(dithiocarboxyl-	tetranine (0.5)	อนอน	
	( ວິ	resin	95		20	(control)

\* less than 0.1 ppm

Example 28.

100 parts of mud, which contained 28ppm of mercury and 38% of water and which was a byproduct of a sodium chloride electrolysis plant, were mixed for 10 minutes with each of several fixing agents, identified by the numbers given in Table

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1, to produce a slurry.

At periods of 1 hour, 1 week, 1 month, 3 months, 6 months and 1 year, 8grs of each of the mixtures were admixed for 5 to 15 minutes with 200ml of pure water or 200ml of diluted aqueous solution of hydrochloric acid of pH8, and the concentration of mercury in the water was measured.

The results are listed in Table 4. 10

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							Мегс	ıry concen	Mercury concentration in water (ppm)	r (ppm)	
fixing agent	agent				Pure water (p)				time		
No.s	(parts)	рпш	water	mixing time	or HCl aqueous		-		£.	9	prof
Table 1	*	(parts)	(parts)	(min.)	solution (HCI)	hour	week	month	months	months	year
	,			Ş	ď	0.003	0.003	0.002	** < 0.001	.0.001	<0.001
	ç.	2	D .	) 	нсі	0.006	0.004	0.004	0.002	0.001	0.001
	·	g	c	ų,	G.	0.005	0.003	6.00.0	0.001	. 0.001	< 0.001
-1	6.5	001	<b>&gt;</b>	<u>a</u>	HCI	0.007	0.005	0.003	0.002	0.001	0.001
	ć	00,	ι	٠,	ď	0.005	0.003	0.003	0.002	0.001	<0.001
Ψ,	U. J	001	C .	n T	нсі	0.008	0.006	0.005	0.002	0.001	0.001
	•	00,	¢	i.	Ь	0.005	0.005	0.003	0.003	0.002	0.001
C	0.1	100	O	CI.	HCI	0.007	500.0	0.004	0.004	0.002	0.002
		90,	c	ı	Ь	0.005	0.003	0.002	0.001	0.001	. 0.001
5	0.1	001	Þ	n	HCI	900'0	0.004	0.003	0.001	0.001	. 0.001
,	. 0	90	c	10	Ω.	0.005	0.004	0.004	0.003	0.001	.0.001
	3	2	>	O.	нсі	0.008	0.005	0.004	0.004	0.002	0.00
α	٠ د	001	C	31	d	0.007	900.0	900.0	0.003	0.002	0.001
	5::5	3	>	Çţ	нсі	0.009	900.0	0.007	0.004	0.003	0.003

TABLE 4 (Continued)

							Maco	TW CORCER	Marchy was a not represented the party of th	r (nom)	
fixing agent	agent		· · · · · · · · · · · · · · · · · · ·				I MET C	מוא במשבכוו	nanon m wan	middy 1:	
Z				mivino	Pure water (p)				time		
in Test l	(parts)	mud (parts)	water (parts)	fine (min.)	HCI aqueous solution (HCI)	four	1 week	1 month	3. months	6 months	l year
ţ	٠,	100		9.	Ъ	0.005	0.003	0.003	0.002	0.001	100.0
	£.0	O. A.	5	0	ווכו	0.006	0.005	0.003	0.003	0.002	0,001
ţ	5	100	5	16	Ь	0.006	0.005	0.003	0.003	0.003	0.002
:	;	6	>		IICI	0.008	0.000	0.005	0.005	0.004	0.003
7	Ē	9	0	9	Ь	0.005	0.005	0.003	0.002	0.001	0.001
			5	2	НСІ	0.006	0.005	0.005	0.004	0.003	0.007
4	0.5	100	c	S	۵	0.005	0.005	0.003	0.003	0.001	0.001
					HCI	9000	0.005	0.004	0.004	0.003	0.007
99	0.3	001	C	=	G.	0.005	0.004	0.004	0.003	0.003	0.001
			,	2	HCI	0.007	0.005	0.005	0.004	0.004	0.003
none(control)	010	100	0		۲	0.030	0.05	0.040	0.055	0.067	0.072
				,	HCI	0.13	0.19	0.22	0.44	0.61	0.75

\* converted into nett content of active ingredient

\*\* ·0.001 means less than 0.001

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Example 29.

100 parts of copper sludge byproduct of a copper electro-plating factory were adjusted to pH7, and 1.0 to 0.5 part of fixing agent (as nett content of effective compound) was added to the sludge and mixed for 10 minutes. Then the sludge was tested by the same method as for Example 28, and the concentration of copper in

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extracting water was measured.

The results are listed in Table 5, in which the fixing agents are identified by the numbers given in Table 1.

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TABLE 5

fixing agent	agent				concentration of copper (ppm)	f copper (ppm)	
)er		copper	mixing		tír	tíme	
in Table 1	(parts)	s ludge (parts)	time (min.)	1 hour	l week	1 month	3 months
5	1.0	100	10	not detected*	not detected	not detected	not detected
3	0.5	100	15	11	11		10
13	0.5	100	01	"			
17	1.0	100	01	11	1,1	:	
30	1.0	100	15	44		r.	
0 (control)	ı	001	0	12	19	17	14 ·

# less than 0.1 ppm

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100 parts of cadmium sludge (containing 13 ppm of cadmium and 73.5% water) by product of a factory using cadmium was adjusted to pH8 and 0.1 to 0.5 parts of fixing agent (as nett content of effective compound) was added to the sludge and mixed for 10 minutes. Then the sludge was tested by the same method as for Example 28 and the concentration of cadmium in extracting water was measured. The results are listed in Table 6.

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TABLE 6

1		T	T		T	1	1	1	7			<del></del>	Ţ	<del></del>	+		
	3 months	0.01	:	:	:	÷	:	:	:	:		:		:	;	:	=
ine	1 month	0.01	÷	:	;	:	:	:	÷	:	1.5	:		:	:	÷	:
	1 week	. 0.01		**	**	;	;	,	;	;	:	:	;		ī	;	
	1 hours	0.01	:	11	4.8	11	:	11	•		:		:	· ·	:		
	test water	water	sea water	water	sea water	water	sea water	water	sea water	water	sea water	water	sea water	water	sea water	water	sea water
mixing	(min.)	01	2	g.				<u> </u>	Ç		2		2	·		Ç	2
cadmium	stunge (parts)	991	Olive Company	100		901		00		901		2		001		3	
	(parts)			ō		6		20		0,1		0.3		0.5		0.5	
number	Table 1	ļķ.		m		-+		90		<b>+</b>		16		17		30	
	cadmium	cadmium mixing time studge time test water i hours I week I month	cadmium mixing   time   studge lime   test water   thours   tweek   thouth   to   to   to   to   to   to   to	cadmium         mixing         time           sludge time         time         1 month           (parts)         (min.)         test water         1 week         1 month           0.1         100         10         water         0.01         0.01         0.01	cadmium         mixing         time         time	cadmium         mixing         fine         time         fest water         1 week         1 month           0.1         100         10         water         0.01         0.01         0.01           0.1         100         sea water         "         "         "           0.1         100         sea water         "         "	Studge   time   test water   thours   tweek   time   test water   thours   tweek   time   test water   thours   tweek   timouth   test water   thours   tweek   timouth   test water   though   to 0.01   to	cadmium         mixing         time         test water         1 hours         1 week         1 mouth           0.1         100         10         water         0.01         0.01         0.01         0.01         0.01           0.1         100         10         water               0.2         100         10         sea water              0.2         100         10         sea water	Studge   time   test water   thours   time   time	Stadge   time   test water   1 hours   time   test water   1 hours   1 week   1 month   test water   1.0   water	cadmium         mixing         time         time           sludge         time         time         1 hours         1 week         1 month           0.1         100         10         sea water              0.2         100         10         sea water              0.2         100         10         sea water              0.3         100         15         water              0.1         100         10         water              0.1         100         10         water	(parts)         time studge time studge time studge time         time test water         1 hours         1 week to not	(parts)         (parts)         (min.)         test water         1 hours         1 week         1 mouth           0.1         100         10         sea water               0.1         100         10         water               0.2         100         10         water               0.2         100         10         water               0.5         100         15         water               0.1         100         10         water               0.1         100         10         water               0.1         100         10         water               0.3         100         10         water	Charts    Char	Charts  charts  chain charts  charts  charts  charts  chain charts  charts  chain charts  charts  chain charts  charts  chain charts  charts	Cadmium   Initial studge   Cantine   Cantine	Cadmium fine   Cast water   C

TABLE 6 (Continued)

fixing agent	agent				cor	icentration of	concentration of cadmium (ppm)	(1)
number		cadmium	mixing	legger feplagje		ţį	time	
in Table 1	(parts)	sludge (parts)	time (min.)	test water	1 hours	l week	1 month	3 months
		00.	d	water	9.0	5.0	1.0	0.5
>	ı	100	<b>D</b>	sea water	8.0	1.1	1.0	0.8

\* <0.01 means less than 0.01

270 parts of soil (containing 20.3 ppm of cadmium and 63% of water) from a paddy field and 1.0 to 0.3 parts of fixing agent were mixed together.

After 3 days, 14 days, 1 month, 3 months and 6 months, 100grs of the soil were treated to the extent that water content was 5%, and 10.0grs of the soil were with 50ml of aqueous solution of citric acid of pH3. The mixture was shaken for 1 hour and the concentration of extracted cadmium in the aqueous solution was measured. The results and fixing agents are listed in Table 7, the fixing agents being identified by the numbers given in Table 1.

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TABLE 7

fixing	agent		concent	ration of ca	dmium (ppm)	· ···· - ···
number in				time	dinium (ppm)	
Table 1	(parts)	3 days	14 days	1 month	3 months	6 months
5	0.5	0.31	0.28	0.27	0.27	0.25
6	0.3	0.56	0.53	0.52	0.51	0.49
8	0.5	0.49	0.48	0.46	0.46	0.45
7	0.3	0.63	0.61	0.59	0.57	0.57
3	0.5	0.23	0.20	0.18	0.19	0.16
1	0.5	0.35	0.31	0.30	0.30	0.28
10	0.5	0.65	0.63	0.63	0.61	0.61
11	0.1	0.74	0.73	0.73	0.71	0.72
12	0.3	0.31	0.28	0.27	0.27	0.26
13	0.3	0.39	0.35	0.32	0.32	0.30
14	0.5	0.3.2	0.31	0.30	0.28	0.28
15	0.5	0.41	0.40	038	0.37	0.37
16	0.5	0.52	0.50	049	0.47	0.48
17	0.5	0.65	0.65	0.63	0.62	0.61
18	1.0	0.58	0.57	0.54	0.53	0.53
19	0.3	0.73	0.71	0.68	0.66	0.65
20	0.5	0.63	0.62	0.60	0.59	0.59
(control)	0	1.2	1.3	1.1	1.2	1.2

Example 32.

Example 32.

Soil (Ohiso-machi Nake-gun Kanagawa-ken Japan) was dried for 11 days at room temperature and for 5 hours at 110°C. 900 grs of the soil were placed in each of a number of pots each of 11.5cm inside diameter and 11cm height, and an aqueous solution of CdSO<sub>4</sub>: 4H<sub>2</sub>O was added to the extent that the total cadmium content in the soil was 20ppm. Then 4 ml of fertilizer containing 120mg of KH<sub>2</sub>PO<sub>4</sub>, 40mg of KCl and 320mg of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and 250ml of water were added to the soil in each pot. After 1 day, 0.003%, 0.03% or 0.3% of a fixing agent was admixed with the soil in each pot. After 4 days, 100 to 200ml of water were added, and 15 grains of rice seeds were planted in the soil in each pot.

of rice seeds were planted in the soil in each pot.

The depths of water in each pot was kept at 2cm above the surface of the soil. Each pot was left for 50 days in a greenhouse under continuous lighting. After 50 days the rice plants were pulled out and washed. The concentration of cadmium in

the roots, or stalks and leaves of the plants was measured.

The results and fixing agents used are listed in Table 8, the fixing agents being identified by the numbers given in Table 1.

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amount of agent		0.0	0.01 %			0.1 %	Po:			1.0 %	≿≍	
	stalks ieaves	S S S S S S S S S S S S S S S S S S S	02	roots	stalks & leaves	र	roots	ıts	stalks leaves	stalks & leaves	100	roots
fixing agent numbers in Table 1	(mda) P.J	inhibi- tion rate (%)	Cd (ppm)	inhibi- tion rate (%)	(p) Cq	inhibi- tion rate (%)	(ppm)	inhibi- tíon rate (%)	(bbm)	inhibi- tion rate (%)	(րբույ	inhibi- tion rate (%)
No. 21	9.7	15	204	20	10.6	7	132	49	9.0	9.5	18	43
No. 22	9.8	14	151	म	6.2	46	108	58	1.4	88	10	96
No. 23	8.0	30	161	326	8.6	25	86	62	1.4	88	5	86
No. 24	11.5	0	198	23	6.9	39	149	85	1.1	90	10	96
No. 25	10.0	12	221	14	6.9	39	7.0	13	1.4	88	13	95
No. 8	9.4	18	170	34	7.9	31	16	62	1.4	88		
No. 15	10.8	2	205	20	4.8	42	184	38	2.1	82		90
(control) none				stalk	s and leav	stalks and leaves: 11.4 ppm		roots: 257 ppm	mqı			
(control) (cadmium was not added)	ium was n	ot added)		stalk	stalks and leaves: 0.5	1	", rc	roots: 4.3	1,			

note: No. 21, No. 22 and No. 25 made leaves deeper green.

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WHAT WE CLAIM IS:-

1. A method of treating a slurry or solution containing heavy metal or heavy metallic compound to fix the metal or metallic compound, comprising the step of mixing with the solution or slurry 0.1 to 50.0% by weight of an aliphatic dithiocarbamate compound, wherein the aliphatic dithiocarbamate compound is a compound having an aliphatic chain, which may contain a nitrogen atom in place of a carbon atom, and at least two dithiocarbamic acid groups

or alkali metal, alkaline earth metal or ammonium hydroxide salts or esters thereof. 2. A method as claimed in claim 1, wherein the aliphatic dithiocarbamate compound is present in a cement composition in an amount of 0.001 to 10% by weight of the composition, and the composition is mixed in the slurry or solution in an

amount of 20 to 80% by weight.

3. A method of treating soil containing heavy metal or metallic compound to prevent plants from absorbing the metal or metallic compound, comprising the step of mixing in the soil 0.001 to 10% by weight of an aliphatic dithiocarbamate compound, wherein the aliphatic dithiocarbamate compound is a compound having an aliphatic chain, which may contain a nitrogen atom in place of a carbon atom, and at least two dithiocarbamic acid groups

(>N-C-S-H) S

or alkali metal, alkaline earth metal or ammonium hydroxide salts or esters thereof. 4. A method as claimed in claim 3, wherein 0.01 to 2.0% by weight of the

compound is mixed with the soil.

5. A method as claimed in any one of claims 1 to 4, wherein the aliphatic dithiocarbamate compound is a compound selected from ethylenedithiocarbamic acids, poly-(dithiocarboxyl)diethylenetriamines, poly(dithiocarboxyl)triethylene tetramines, poly-(dithiocarboxyl)tetraethylenepentamines and alkali metal or alkali earth metal salt of these amines.

6. A method as claimed in any one of claims 1 to 4, wherein the aliphatic dithiocarbamate compound is selected from propylenedithiocarbamic acids, poly(dithiocarboxyl) dipropylene triamines, poly(dithiocarboxyl) tripropylenetetramines, poly(dithiocarboxyl)tetrapropylenepentamines poly(dithiocarboxyl) and

propylenehexamines. 7. A method as claimed in any one of claims 1 to 4, wherein the compound is prepared by reacting amines selected from ethylene diamine, diethylene triamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, propylenediamine, dipropylene triamine, tripropylenetetramine, tetrapropylenepentamine and pentapropylenehexamine with carbon bisulfide, one gram molecule of amine to 2 to 6 gram

molecules of carbon bisulfide being employed. 8. A construction cement having a heavy metal or heavy metallic compound fixing agent, the agent being present in an amount of 0.001 to 10% by weight and comprising a compound prepared by reacting an amine selected from ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine,, propylenediamine, dipropylene triamines tripropylene tetramine, tetrapropylene pentamine and pentapropylenehexamine with carbon bisulfide, one gram

molecule of amine to 2 to 6 gram molecules of carbon bisulfide being employed. 9. A method as claimed in any one of claims 1 to 4, wherein the compound is prepared substantially as hereinbefore described with reference to any one of Examples

1 to 25.

10. A method as claimed in claim 1, substantially as hereinbefore described with reference to either Example 26 or Example 27.

11. A method as claimed in claim 1, substantially as hereinbefore described with

reference to any one of Examples 28 to 30.

12. A method as claimed in either claim 3 or claim 5, substantially as herein-55 before described with reference to either Example 31 or Example 32.

DR WALTHER WOLFF & CO., 75, Victoria Street, London, S.W.1, Chartered Patent Agents, Agents for the Applicants.

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